

Development of Advanced SCR Catalysts

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OBJECTIVES

Nitrogen oxide (NO_x) emissions from combustion processes are a significant environmental problem because they contribute to photochemical smog formation and acid rain. In addition, some NO_x compounds, notably N_2O , are persistent greenhouse gases. Treatment of NO_x compounds in combustion flue gases is difficult because they are dilute, with typical NO_x concentrations on order of 1000 ppm. Current flue gas NO_x abatement technologies known as Selective Catalytic Reduction (SCR) depend on heterogeneous catalysts that require addition of reductants, such as ammonia, hydrocarbons, or carbon monoxide. Direct NO_x decomposition catalysts are desirable to decrease operating costs and improve performance compared to existing SCR systems.

Cobalt oxide (Co_3O_4) with small amounts of alkali metals has been shown to be effective direct NO_x decomposition catalysts. However, the previously reported catalysts were unsupported, with low surface areas (less than $38 \text{ m}^2/\text{g}$). The objective of this project is to develop new direct NO_x decomposition catalysts that are both effective and stable in coal combustion flue gases. Supported cobalt oxide with alkali metal catalysts are being developed in an effort to achieve this objective.

ACCOMPLISHMENTS TO DATE

A series of catalysts with varying amounts (1, 2, 5, 10, and 15 wt%) of cobalt oxide (CoO_x) and an alkali metal (lithium, sodium, potassium, rubidium, or cesium incorporated in 0.01, 0.035, and 0.05 alkali:Co atomic ratios) supported on γ -alumina have been synthesized for this project. A flow microreactor, with a mass spectrometer for product analysis, was constructed and is being used to test these heterogeneous catalysts. Preliminary results show that the $\text{Rb-CoO}_x/\text{Al}_2\text{O}_3$ catalysts are approximately 20 times more active per gram than the corresponding unsupported catalysts that have been previously reported. At a reaction temperature of 920 K, the preliminary results also show that 62% of 1000 ppm NO in nitrogen can be decomposed to nitrogen and oxygen at a gas hourly space velocity (GHSV) of 120,000, which are respectively ~5% higher conversion and 17 times higher space velocity than previously reported results. The catalysts appear to be effective over a range of temperatures (773-923 K), although high temperatures (>873 K) appear to be necessary to reduce more than 50% of the NO_x under the experimental

conditions examined. Experiments are continuing using catalysts with a range of cobalt oxide surface densities to confirm the preliminary results.

FUTURE WORK

The remainder of the promising catalysts will be kinetically tested in the microreactor to examine the dependence of NO_x decomposition rate, normalized per cobalt and alkali metal atom, as a function of surface density of CoO_x and alkali. Reaction rates normalized per atom of active catalyst have been shown to vary by over a factor of ten as a function of active metal oxide surface density for other reactions. The hypothesis of this work is that similar trends will be observed for NO_x decomposition catalysts and that more active catalysts will be discovered. The catalysts will be characterized using physisorption techniques to measure surface area and UV-visible spectroscopy to determine the relation between edge energy, which corresponds with the size and type of surface domains of CoO_x on the catalysts, and catalytic performance. In situ UV-visible spectroscopic experiments of the catalysts during NO_x decomposition will be performed to investigate the mechanism of the surface reactions and to provide insight for future catalyst improvements.

LIST OF PAPERS PUBLISHED, U.S. PATENTS/PATENT APPLICATIONS, CONFERENCE PRESENTATIONS, AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH, AND STUDENTS SUPPORTED UNDER THIS GRANT

“In situ UV-visible spectroscopic studies of supported metal oxides during catalytic oxidation of alkanes and NO_x decomposition.” Presentation at the American Chemical Society Spring 2005 National Meeting in San Diego, CA, March 15, 2005.

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